

COMETS, CARBONACEOUS CHONDRITES, AND INTERSTELLAR
CLOUDS: CONDENSATION OF CARBON

G. B. Field
Center for Astrophysics
60 Garden Street
Cambridge, Massachusetts

SUMMARY

Dark interstellar clouds are known to contain silicate particles, and are suspected to contain graphite particles. Mantles of tarry material condensed in circumstellar winds and/or mantles of complex organic compounds, produced by photolysis of ice mantles in diffuse interstellar clouds, may also be present. It is believed that in addition ice mantles of CH_4 , NH_3 , and H_2O are present in dark clouds.

Direct formation of comets from such particles would result in a mixture of dust and ice not unlike that inferred from observations of comets, so it seems plausible that such was the case. However, the presence of ^{13}C -poor graphite would suggest that cometary gases are enriched in ^{13}C , contrary to available spectroscopic observations of $^{13}\text{C}/^{12}\text{C}$. As the alternative of heating the material from which comets were made to the point that graphite would evaporate seems implausible, doubt is thrown upon the existence of graphite in interstellar clouds at least if it is ^{13}C -poor. Any measurements which address the various possible forms of carbon in comets (graphite, tars, organic molecules, methane) would help elucidate this question, as would further measurements of $^{12}\text{C}/^{13}\text{C}$ in various gas-phase molecules.

COMETS

All the evidence supports Whipple's theory that the nucleus of a comet consists of a loose collection of ices and dust. Infrared observations prove that silicate dust is present; spectroscopic observations, particularly of H , OH , H_2O , and H_2O^+ , indicate that water ice is a major constituent. Observations of CH , C_2 , C_3 , and other carbon-bearing molecules prove that carbon is present. Analysis of the production of gas by comets

indicates that the carbon may be bound in the ice in the form of CH_4 clathrate. The fact that the cometary cloud extends to interstellar distances and that comets contain volatiles which can condense only at great distances from the sun suggests that cometary material may provide a bridge between planetary material, which condensed within the solar system, and the dust in interstellar clouds.

CARBONACEOUS CHONDRITES

The carbonaceous chondrites are characterized by low density, high carbon content (up to 5%), and a grainy structure which shows very little metamorphism. They seem to be formed of silicate and iron minerals which condensed into dust particles directly from the gas of the solar nebula as it cooled.

The bulk of the carbon in these objects is in the form of tarry material between the silicate grains. It is relatively insoluble, but the small soluble fraction has been found to contain complex organic molecules of every description, including amino acids (Anders 1971).

According to thermodynamic equilibrium calculations, various silicate and iron minerals condense out sequentially as a gas of cosmic composition is cooled (Table 1). These calculations have been very successful in accounting for the observed mineral morphology. However, the presence of carbon compounds does not follow from strictly equilibrium considerations, and the theory which accounts for them remains controversial. We will return to this topic below.

CLOUDS

Interstellar clouds come in all shapes and sizes (Figure 1). In the dark clouds, seen in photographs projected against background stars, the

Table 1. Condensation temperatures for the case $C < 0$

Stage	Temperature (°K)	Condensates	Elements Removed
1	1400-1600	CaTiO ₃ Mg ₂ Al ₂ O ₄ , Al ₂ SiO ₃ , CaAl ₂ Si ₂ O ₈ CaMgSi ₂ O ₆ , Ca ₂ SiO ₄ , CaSiO ₃	Ti Al Ca
2	1220-1320	MgSiO ₃ , Mg ₂ SiO ₄ , BeAl ₂ O ₄	Si, Mg, Be
3	1280	Metallic Fe, Ni	Fe, Ni
4	1210	MnSiO ₃	Mn
5	970-1070	Alkali Silicates	Na, K, Rb
6	600-700	FeS, NaBO ₂	S, B
7	180	H ₂ O	O
8	120	NH ₃ · H ₂ O	N
9	75	CH ₄ · XH ₂ O	C
10	25	Ar (solid)	Ar

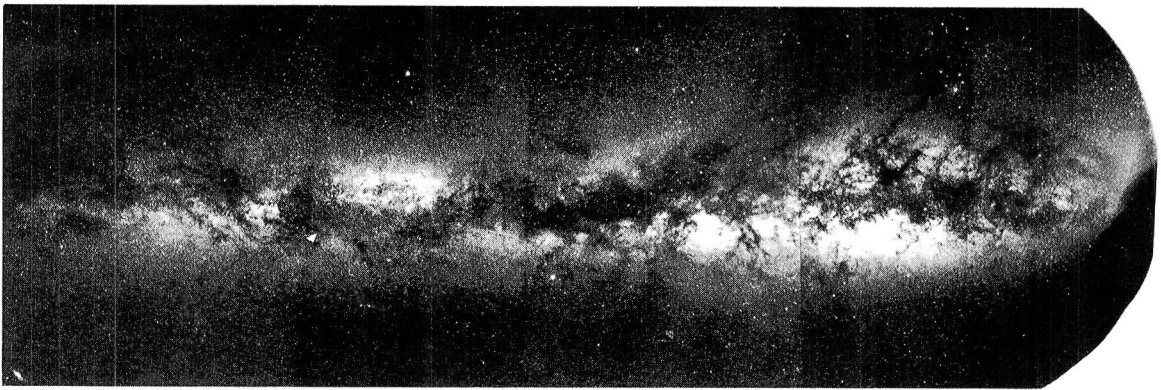


Fig. 1. A composite photograph of the Milky Way, showing the system of stars we see passing overhead, heavily obscured at places by intervening clouds of interstellar dust.
(Hale Observatories)

most abundant element, H, is in the form of H_2 molecules. Although helium and the other noble gases are in the atomic state, it is believed that most other elements are condensed into the dust particles which cause the observed blocking of starlight. A small fraction of the C, N, and O forms molecules which can be observed by the spectral lines they emit in the microwave region.

If the density of an interstellar cloud is low enough to let in starlight, however, the H_2 is photodissociated to atomic H (Spitzer 1978). Other molecules are also largely photodissociated into their atomic constituents, so radio astronomers can detect molecules in such clouds only with difficulty. On the other hand, the cloud is so diffuse that stars can be seen through it, and atoms can be detected via the absorption lines they impress on the stellar spectra.

Ultraviolet observations of diffuse clouds with the Copernicus satellite have established that many elements (silicon, magnesium, iron, calcium, aluminum, titanium) are severely depleted (10-1000 times) in the gas phase (Figure 2). This agrees well with the fact that the dust absorption exhibits a band at 10μ wavelength, as predicted for silicate dust, for these are just the elements which are expected to form silicate dust. The same silicate feature is seen in dark clouds, confirming that there is silicate dust there as well (Figure 3). The atomic depletion cannot be tested in dark clouds because ultraviolet and visible starlight cannot be seen through such clouds; however, infrared does get through, enabling us to study the $10\text{-}\mu$ band.

Some 40 molecules have been detected in dark clouds, about 30 of them containing carbon (Table 2). CO, the most abundant, appears to contain only about 10% of the C, and other molecules are even less abundant in

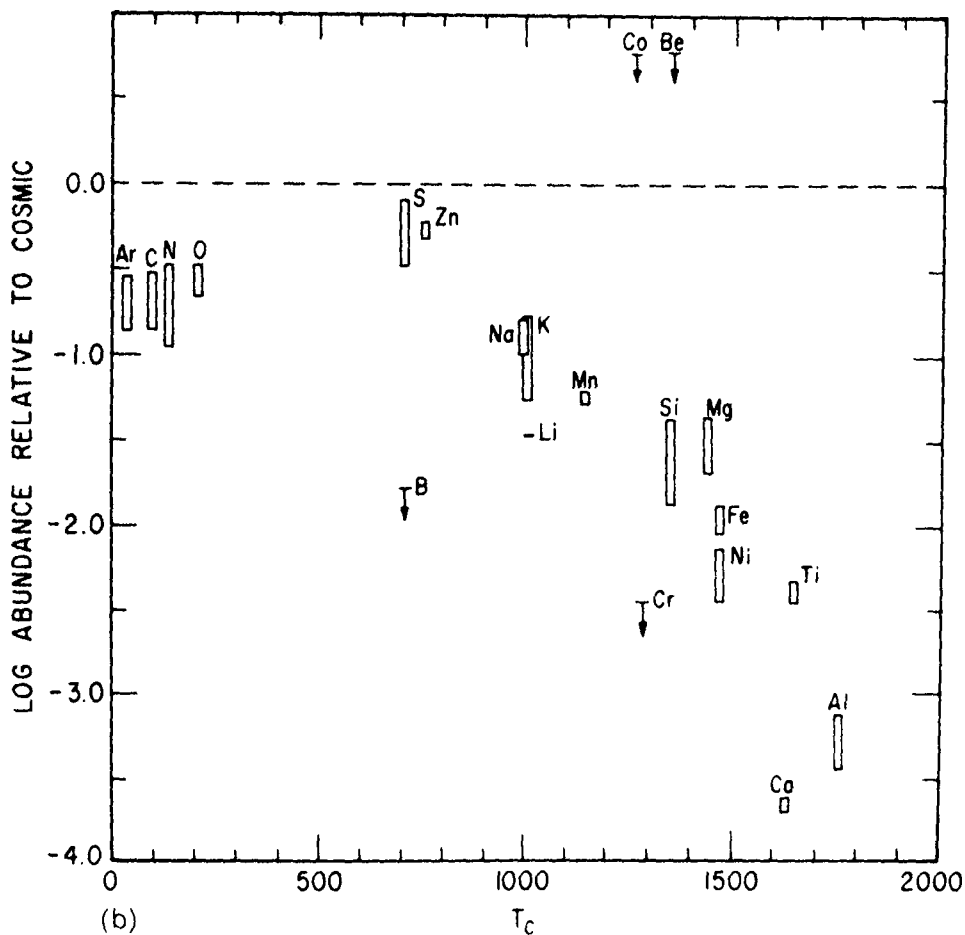


Fig. 2. Abundances of gas-phase atoms and ions in the diffuse interstellar clouds between the earth and the star Zeta Ophiuchi about 170 parsecs distant, according to studies conducted by Morton (1974), at Princeton using the ultraviolet spectrometer on the Copernicus satellite. Abundances are plotted logarithmically relative to those in the sun, so that zero ordinate (--) means normal abundances, and -1.0 means depletion by a factor 10. The abundances are plotted against the temperatures T_c at which the elements would condense out if $C < 0$ according to Table 1. Note the rough correlation of the depletion factors with increasing T_c above 700°K.

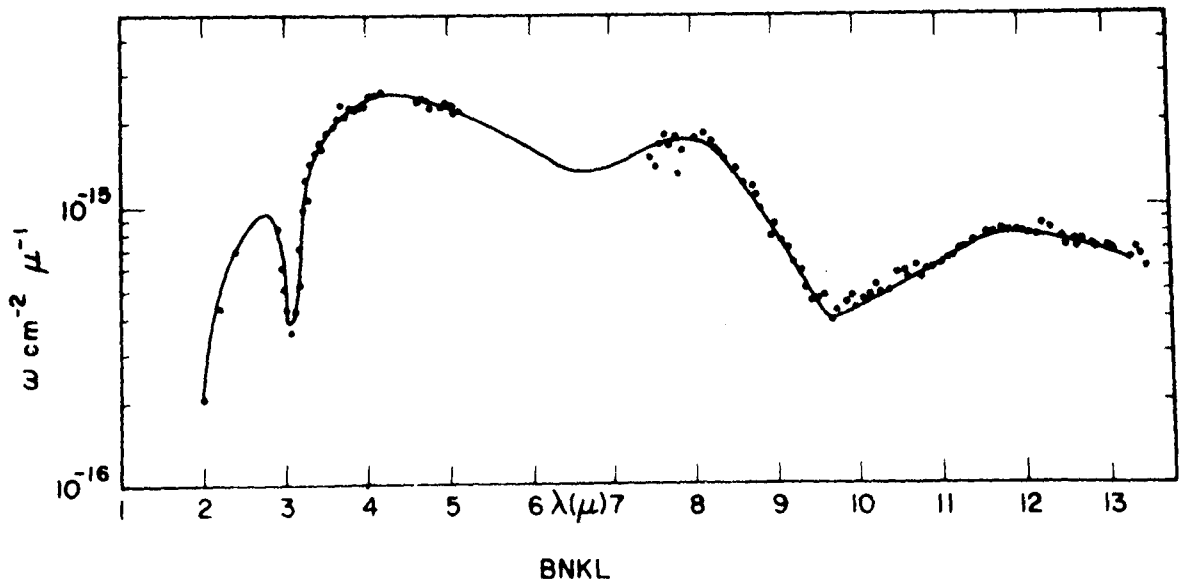


Fig. 3. The spectrum of the infrared source in Orion, showing characteristic absorption features at 3.1 μ (attributed to water ice) and 10 μ (attributed to silicates).

Table 2. Molecules detected in the interstellar medium as of 1977
(Field, Verschuur, and Ponnampertuma, 1978)

Observed in Interstellar Space	Name
H ₂	Hydrogen
CH ⁺	Methylidyne ion
CH	Methylidyne radical
CN	Cyanogen
OH	Hydroxyl radical
CO	Carbon monoxide
CS	Carbon monosulfide
SiO	Silicon monoxide
NS	Nitrogen sulfide
SO	Sulfur monoxide
SiS	Silicon sulfide
H ₂ O	Water
HCN	Hydrogen cyanide
HNC	Hydrogen isocyanide
HCO ⁺	Formyl ion
H ₂ S	Hydrogen sulfide
OCS	Carbonyl sulfide
SO ₂	Sulfur dioxide
C ₂ H	Ethynyl radical
N ₂ H ⁺	(Unnamed)
HDO	Heavy water
NH ₃	Ammonia
H ₂ CO	Formaldehyde
H ₂ CS	Thioformaldehyde
HNCO	Isocyanic acid
C ₂ H ₂	Acetylene
HCOOH	Formic acid
H ₂ CNH	Methanimine
HC ₃ N	Cyanoacetylene

Table 2. Molecules detected in the interstellar medium as of 1977
(Field, Verschuur, and Ponnampertuma, 1978) (Continued)

Observed in Interstellar Space	Name
H_2NCN	Cyanamide
CH_3OH	Methyl alcohol
CH_3CN	Methyl cyanide
NH_2HCO	Formamide
$\text{CH}_3\text{C}_2\text{H}$	Methylacetylene
CH_3HCO	Acetaldehyde
CH_3NH_2	Methylamine
$\text{H}_2\text{C}_2\text{HCN}$	Vinyl cyanide
HC_5N	Cyanodiacetylene
HCOCH_3	Methyl formate
$\text{CH}_3\text{CH}_2\text{OH}$	Ethyl alcohol
$(\text{CH}_3)_2\text{O}$	Dimethyl ether

relation to their parent atoms. While H_2 is catalyzed on grain surfaces, it is believed that most other molecules are formed by gas-phase, ion-molecule reactions involving H_2^+ , which in turn is formed by the cosmic-ray ionization of H_2 (Figure 4). Chemical schemes embodying these reactions have had a number of successes, the latest being the prediction of the abundance of C_2 .

CARBON IN STARS

In the solar system and in the atmospheres of normal stars, $C/H = 3.7 \times 10^{-4}$ and $O/H = 6.7 \times 10^{-4}$ (Cameron 1973). Thus, $C/O = 0.55$. The $^{13}C/^{12}C$ ratio in the solar system is 1/90. This ratio seems to apply in many stars, but in others the ratio appears to be higher.

Carbon is produced in stars in two ways, as a byproduct of the CNO cycle in stars like the sun, and as a product of helium burning (triple α) in the hot cores of giant stars. Theoretically, these two processes are easily distinguishable: the CNO cycle gives $C < 0$ and $^{13}C/^{12}C$ ranging up to 1/4, while 3α gives $C > 0$ and $^{13}C/^{12}C \ll 1$. Unfortunately, the effects of both processes are sometimes confused in the same type of evolved star, the outer layers showing the effects of an earlier CNO phase and the inner layers, exposed by mass loss, showing the effects of 3α .

Although normal stars and the interstellar medium as a whole have $C < 0$, some special stars have $C > 0$. Among these are carbon stars, infrared stars believed to be the precursors of planetary nebulae, and planetary nebulae themselves (Figure 5).

Thermodynamics predicts dramatic chemical effects when one switches from $C < 0$ to $C > 0$ because of the great stability of the CO molecule. Thus, when $C < 0$ (the usual situation), cooling below about 3000° produces

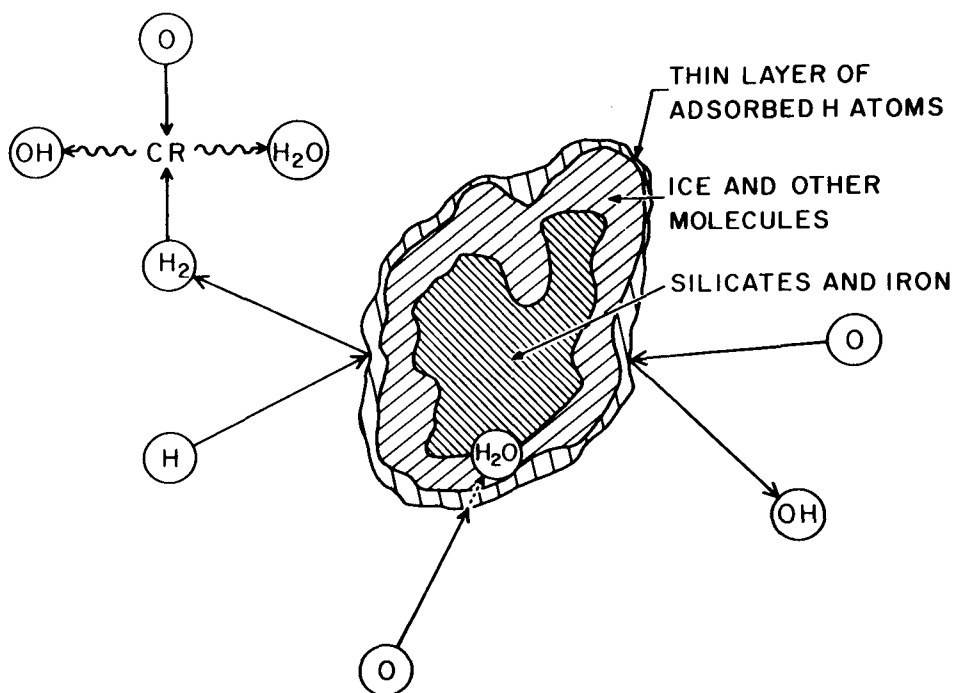


Fig. 4. An artist's conception of an interstellar grain. H_2 is formed by surface reactions among adsorbed H atoms, and expelled into the gas. Cosmic rays produce H_2^+ , which reacts with C, N, and O to give OH, H_2O and other molecules of Table 2. OH can also be produced directly by surface reactions of O and H, and the H_2O produced in this way (as well as CH_4 and NH_3) freezes down to provide an ice mantle.

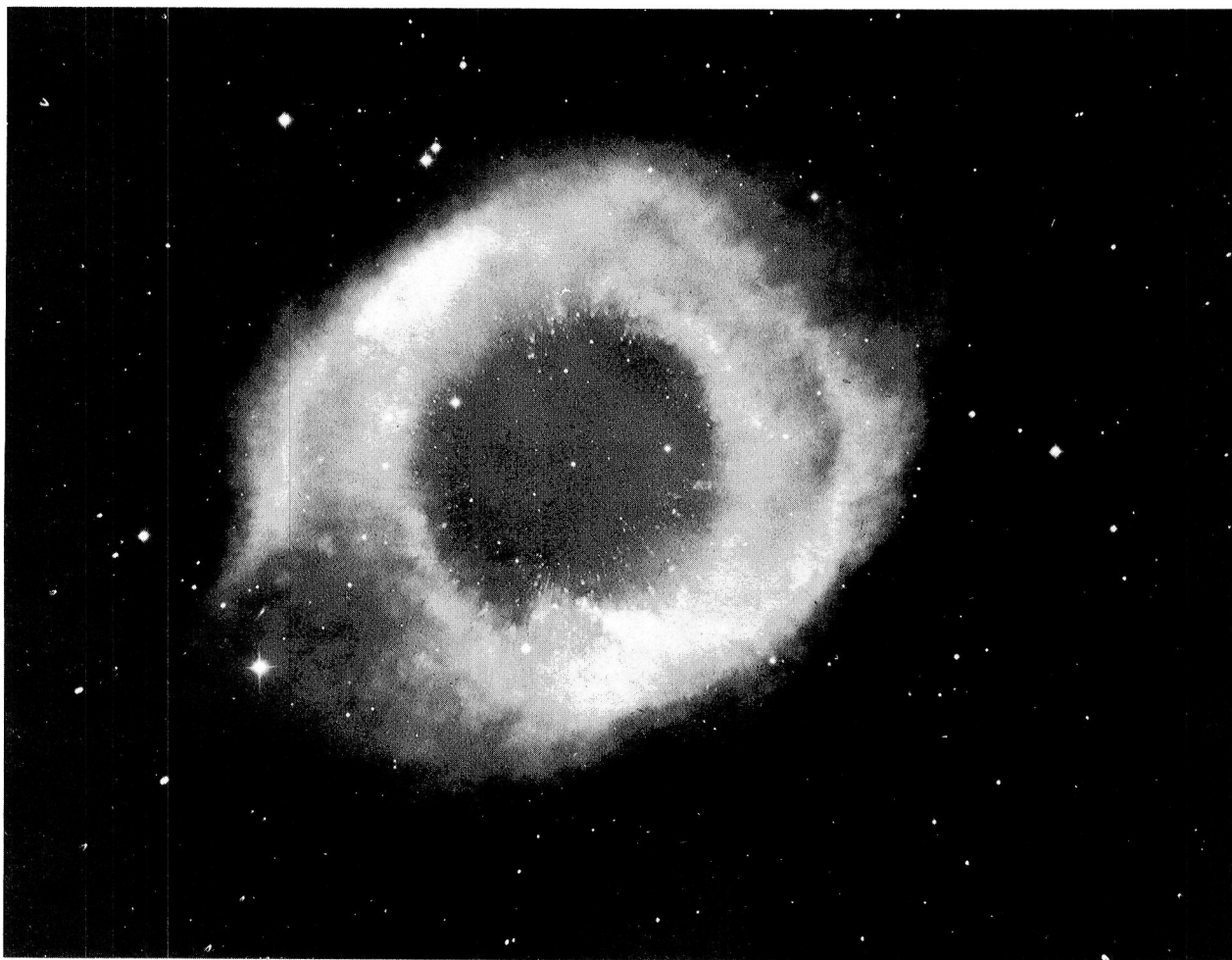


Fig. 5. A planetary nebula. The central star, a compact hot star left over after the expulsion of the outer layers of a giant star to form the nebula, can be seen. (Hale Observatories)

CO, with the extra O going into H_2O . When $\text{C} > \text{O}$, carbon is left over, and instead of H_2O , one gets carbon-bearing molecules like C_2 . When the temperature drops low enough (say $< 2000^\circ$), very different condensation processes occur. If $\text{C} < \text{O}$, oxygen is available to make silicates, and carbon remains gaseous as CO. If $\text{C} > \text{O}$, all the O is in CO, and the excess carbon condenses as silicon carbide (SiC) and graphite.

Both O-rich and C-rich giants have been observed to undergo mass loss. As might be expected, the cooling of the expanding gas promotes formation of dust in these cases. In the O-rich giants one sees dust, which, because of the presence of the $10\text{-}\mu$ feature, must contain silicates. In the C-rich giants one also sees dust, but no $10\text{-}\mu$ feature. The dust is presumed to be graphite and silicon carbide.

The interstellar medium is the ultimate repository of stellar dust. As stated earlier, silicate dust is observed to be ubiquitous there. In view of the fact that C-rich stars are observed to emit dust which is known not to be silicate, it is interesting to ask whether graphite can be seen in the interstellar medium. Graphite has no infrared features, and thus cannot be detected in the cool stars where it is believed to be forming. However, it does have a very strong ultraviolet absorption band at 2200 \AA , due to transition of a π electron into the conduction band. On this basis it was predicted (Hoyle and Wickramasinghe 1962) that this band should appear in interstellar extinction. This prediction was dramatically confirmed by the OAO-2 satellite, which found that the 2200 \AA band appears in nearly every star, with a strength proportional to the amount of extinction in the visible (Figure 6). From these observations one calculates (Field 1974) that in the diffuse clouds 60% of the carbon is in graphite.

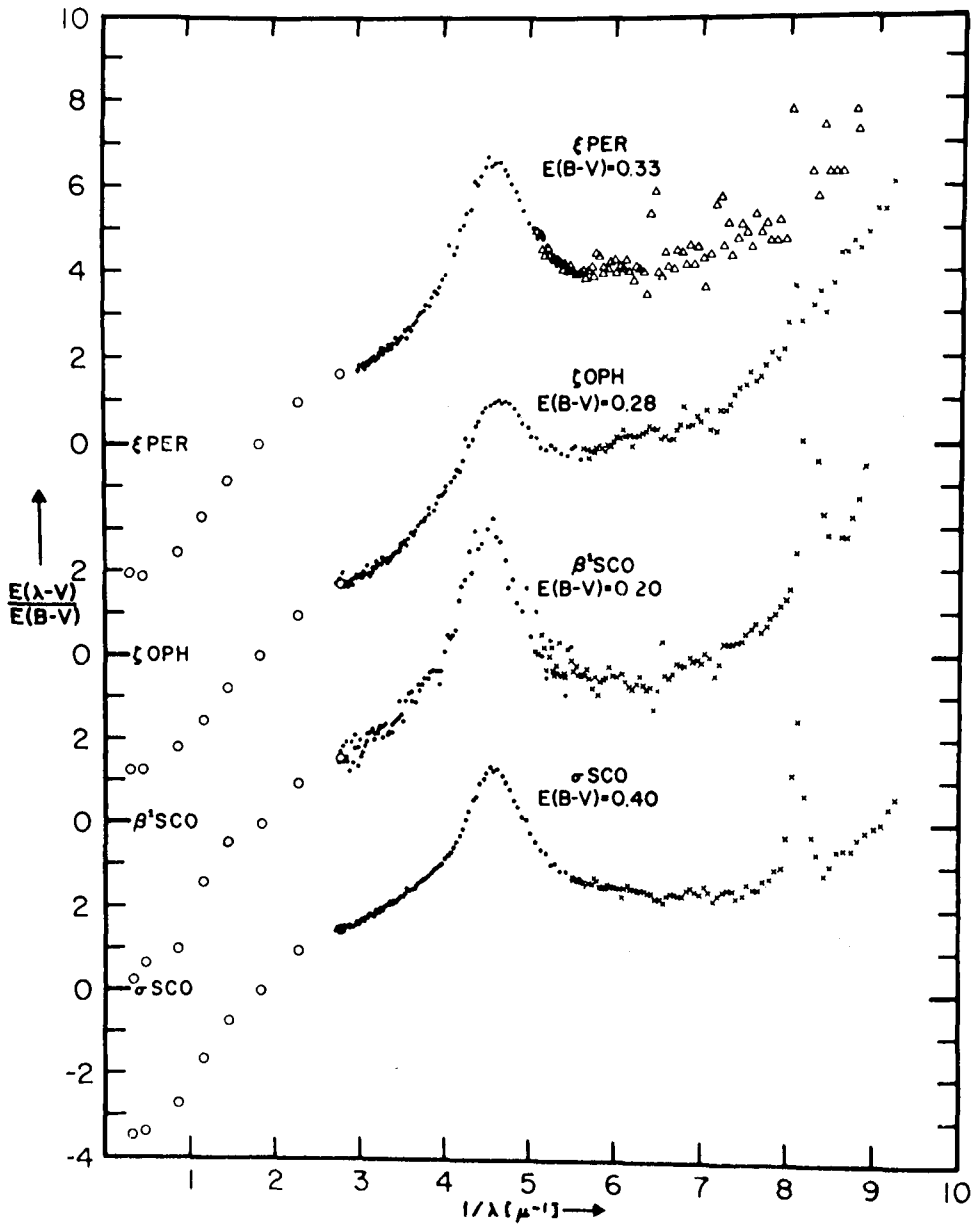


Fig. 6. Evidence for graphite in the interstellar medium. What is plotted is the attenuation of various stars, in magnitudes, against wave number in inverse microns. The absorption feature at $\lambda^{-1} = 4.5 \mu^{-1}$ ($\lambda = 2200 \text{ \AA}$) is characteristic of graphite (Bless and Savage 1972).

CARBON IN CLOUDS

What is the state of the ~40% of the carbon in diffuse clouds which is not in graphite? The Copernicus satellite found that, like silicon, magnesium, etc., the volatile elements C, N, and O are also depleted from the gas phase, typically by factors 3-5. Although both the graphite and gas-phase abundances are uncertain, it seems likely that carbon has condensed in forms other than graphite, as well as into graphite. As the graphite must have formed in C-rich stars, the remaining fraction must contain that carbon which was ejected, along with silicate dust, from O-rich stars. Any molecular components like CO in such ejecta would have been photodissociated as soon as the ejecta became optically thin; indeed, Copernicus observed very little CO in diffuse clouds. Two possibilities present themselves:

(i) During ejection from the star, carbon condensed onto grains in the form of the tarry material found in carbonaceous chondrites. We will discuss this process further below, but suffice it to say here that this would explain how it avoided being returned to the gas phase, as the material should be resistant to photodesorption.

(ii) Alternatively, (i) did not happen with any regularity, and the carbon was slowly accreted by the grains much later, while in the interstellar medium. This takes us back to the original proposal by Oort and van de Hulst (1946) - that the interstellar atoms of C, N, and O would stick to grains, and because of the great abundance of H, form a composite ice of CH_4 , NH_3 , and H_2O .

While this is an attractive picture, it must be modified to agree with current facts. First, it is known from laboratory work that such

a mixture exposed to the UV spectrum of interstellar space would be photolyzed in 10^6 years (Greenberg *et al.* 1972). The resulting material should contain free radicals and the products of their reactions together--organic molecules of every description. Second, and quite harmonious with this fact, H₂O ice has been sought in diffuse clouds by means of its 3.1- μ absorption band, without success; less than 10% of the O can be in this form. If the icy mixture were photolyzed, the ice band would not be present, as is observed to be the case. Against this picture, however, are calculations which show that volatiles are readily removed from silicate grains by photodesorption. How do the ices form in the first place?

It should be noted that relatively weak shock waves occurring in the interstellar medium will result in the sputtering of a volatile mantle off the dust grains. The Copernicus satellite observations of small amounts of gas-phase C, N, and O would allow perhaps one in five clouds to have been recently processed in this way.

In summary, C (also N and O) is depleted over and above that C in graphite. It could be in the form of a tarry mantle which accompanied the formation of silicate dust, or in the form of photolyzed mantles of CH₄, NH₃, and H₂O ices. Identification of the many diffuse interstellar bands, believed to originate in the solid phase, but not so far identified with any mineral, could bear on this question, as the organic molecules postulated to be in the mantles seem to be reasonable sources for such bands.

The dark clouds are colder and denser than the diffuse clouds; molecules, once formed, are safe from photodissociation, and atoms and molecules sticking to dust grains are safe from photodesorption. Where, then, is the carbon? The opacity of dark clouds prevents complete spectroscopic studies, so we

don't know the amount of graphite or of gas-phase carbon atoms or ions. However, the masses of such clouds are so great ($\sim 10^5 M_{\odot}$) that the material in them must be the product of a large number of stars, and must be gathered in from a large region of interstellar space. Hence it is reasonable to suppose that they have formed from more diffuse material, perhaps by gravitational accretion. In the process, the graphite grains would be expected to be dragged along unchanged.

CO and other C-bearing molecules are observed, but they do not account for all the remaining C. Klemperer (1978) has pointed out that for the gas phase ion-molecule chemistry to produce the molecules we see, the gas phase must not be oxygen rich; that is, $C \geq O$ in the gas phase. This is an important point, if true, because it bears on the question of where the O is. In view of the fact that non-graphite C is only 1/5 of total O (40% of 0.55), the removal of O must be nearly complete to drive C above O in the gas phase.

In dark clouds ice mantles seem like a good bet. Not only does photo-desorption fail to prevent them, but the H_2O ice band has actually been detected in a number of dark clouds. A plausible hypothesis would be that all the C and O which is not in CO has frozen down in a classical ice of CH_4 , NH_3 , and H_2O . CO itself is very volatile and is not expected to freeze down at the temperatures of the dust in dark clouds ($\sim 10^\circ K$). Presumably the CO formed from the gas-phase C and O known to be present in the diffuse clouds at 20-30% of the total abundance.

In summary, the dust in dark clouds may well have ice mantles as well as mantles of tarry material and/or photolyzed ices carried over from diffuse clouds.

An interesting sidelight in all this is the $^{13}\text{C}/^{12}\text{C}$ ratio. As we said earlier, this ratio is expected to depend upon the source of the carbon (CNO or 3α). Normally one would expect that carbon from both sources would be well mixed throughout the interstellar medium. Observations of stars which have formed from the medium demonstrate that this is the case where different elements are involved. Hence the ^{12}C and ^{13}C in the solar system as a whole should represent contributions from both sources. As a result, the measured $^{13}\text{C}/^{12}\text{C}$ ratio in the earth and meteorites (1/90) should be indicative of the overall ratio in the interstellar medium at the time the solar system formed.

However, graphite could introduce an interesting wrinkle in this. If it formed in C-rich stars, which are carbon-rich because of 3α , it would contain little ^{13}C , so that the non-graphite fraction of the interstellar medium must contain most of the ^{13}C . If the graphite is 60% of the interstellar carbon, and if its $^{13}\text{C}/^{12}\text{C}$ is $\ll 1/90$, the remaining fraction must have $^{13}\text{C}/^{12}\text{C} \approx 1/36$. It is interesting that Townes (1977) in his 1976 Halley Lecture concludes from a large amount of data on carbon-bearing molecules in dark clouds that $^{13}\text{C}/^{12}\text{C}$ in those molecules is roughly a factor of two higher than 1/90. On the other hand, there is reason to be skeptical of this result. Not only are there severe saturation problems with many of the lines observed, but Watson (1973) has proposed that chemical fractionation can account for the observed effects, if real. Moreover, an optical observation of $^{13}\text{CH}^+$ in front of ζ Oph, in which saturation effects should be easier to account for, yields $^{13}\text{C}/^{12}\text{C} = 1/(90 \pm 30)$ (Snell *et al.* 1977). As the ratio for CO in the same star equals $1/(80 \pm 25)$ there is no direct evidence for fractionation between these molecules, while the theory suggests there should be a factor of 2 difference.

How would the lack of ^{13}C in interstellar graphite (if true) affect the solar system? Because graphite is highly refractory, it would certainly survive incorporation into cometary material, so again one would expect ^{13}C enrichment of the non-graphite fraction. Although the observations are quite uncertain and involve only one molecule (C_2) in three different comets; they all give $^{13}\text{C}/^{12}\text{C} \approx 1/100$ (Whipple and Heubner 1976), apparently sufficient to exclude much graphite in comets if indeed it is poor in ^{13}C .

In this connection, it is interesting to inquire into the $^{13}\text{C}/^{12}\text{C}$ ratio in carbonaceous chondrites. The overall ratio is 1/90, although some fractionation is seen among the various molecules, which can be explained by normal chemical processes. There seems to be disagreement as to whether graphite is or is not present; if so, it is certainly a small fraction of the carbon. According to one study (Vinogradov et al., 1967), $^{13}\text{C}/^{12}\text{C}$ in the graphite is 1/91, not significantly different from the overall ratio. Of course, it is conceivable that small amounts of graphite formed later from the tarry material, in which case no gross effects are expected.

CARBON IN METEORITES

This brings us to a general discussion of the carbon in carbonaceous chondrites. We alluded above to the fact that chemical equilibrium calculations yield a condensation sequence which seems to account for the minerals in the grains of carbonaceous chondrites in a straightforward way by cooling from a high temperature. However, carbon is a different story. It is found that in the presence of large amounts of H_2 , the stable form of C is CO above about 600°K, but CH_4 below that temperature. As CH_4 does not freeze out until 75°K, if this were the whole story C

would be gaseous (CO or CH_4) within the inner solar system, and therefore would not have been incorporated into the terrestrial planets (or meteorites), as is demonstrated from the near absence of the noble gases from the earth. How, then, is one to account for the abundant carbon on the earth and in carbonaceous chondrites? Anders (1971) answers that although CH_4 is thermodynamically stable below 600°K , the reaction $\text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}$ by which it is produced from CO goes very slowly in the absence of catalysts. Suitable catalysts are not present at 600°K , but at 350°K , iron oxidizes to Fe_3O_4 and the silicates take on water of hydration; both products are good catalysts. However, the ensuing reactions do not reduce the carbon entirely to CH_4 , but only about halfway, to hydrocarbons of the type $\text{C}_{20}\text{H}_{42}$. These latter have high molecular weight and low vapor pressure, and hence condense out on the dust particles already present in the solar nebula. The process is similar to the Fischer-Tropsch synthesis used commercially to produce gasoline. By way of proof, Anders shows that many of the compounds and their detailed properties (e.g., $^{13}\text{C} - ^{12}\text{C}$ fractionation) found in carbonaceous chondrites match very well those found in the laboratory using Fischer-Tropsch synthesis. If this is the correct picture, carbon is present on the earth only because of a quirk in reaction kinetics which produced high-molecular weight hydrocarbons instead of CH_4 .

CARBON IN COMETS

What, then, of the comets? The presence of H_2O ice in them shows that they could not have accumulated at temperatures above 200°K , or else the ice would have sublimed and been lost (as indeed it is observed to do when comets enter the inner solar system). On the other hand, we

don't know the maximum temperature reached by cometary material. If $> 2000^\circ\text{K}$, everything would have been vaporized, and the standard condensation sequence would have been followed. In this case, one would expect at least some of the carbon to have produced a Fischer-Tropsch tar at $\sim 350^\circ\text{K}$. As the temperature fell, H_2O would ultimately have condensed out as ice. It is not clear whether enough carbon would have remained to produce the CH_4 believed to be responsible for the clathrate needed to explain the observed properties of comets. In this model, perhaps even the graphite would have been vaporized, and so no gross anomalies in $^{13}\text{C}/^{12}\text{C}$ would be expected.

Suppose, on the other hand, that the highest temperature is in the range $500^\circ - 2000^\circ\text{K}$, say. Then the refractories (including graphite) in the interstellar dust would have survived, while the volatile mantles (be they tar or ices) would have evaporated. In this case, Fischer-Tropsch would again produce tar, but its $^{13}\text{C}/^{12}\text{C}$ would be anomalous; when CH_4 freezes out at lower temperatures, its $^{13}\text{C}/^{12}\text{C}$ would be anomalous also. The spectroscopic observations of $^{13}\text{C}/^{12}\text{C}$ in comets argue against this case.

If T_{max} is in the range $200 - 500^\circ\text{K}$, the tars as well as the refractories would survive, but ices would have evaporated, only to recondense when T dropped below 200° . The $^{13}\text{C}/^{12}\text{C}$ ratio is still inconsistent with observation.

Finally, if $T_{\text{max}} < 200^\circ\text{K}$, even H_2O ice would survive, and if T_{max} is low enough, CH_4 ice would also. Because these substances are expected to be major components of dense interstellar clouds (see above), cometary material would be expected to be a mixture of ice and dust, as is observed. Again, however, the $^{13}\text{C}/^{12}\text{C}$ ratio would be anomalous, contrary to observation.

If one takes these considerations seriously, only the high-temperature model is allowed; only in that model is the graphite vaporized and its low ^{13}C content distributed. However, there are severe objections to the high-temperature model. According to models of the solar nebula, high temperatures never prevailed outside the inner solar system. Hence, the high-temperature scenario requires that comets form in the inner solar system, and hence have small perihelia. But then they would long ago have become periodic or hyperbolic as a result of planetary perturbations. Instead, it is believed that the comets formed far from the sun, where the temperatures are low, and that the long-period ones are entering the solar system for the first time as a result of stellar perturbations. Thus, one would expect them to consist of unprocessed interstellar grains, which as we have seen should be a mixture of silicates, graphite, and mantles of tar and ice. This seems to accord well with what we know about comets, with the exception of the $^{13}\text{C}/^{12}\text{C}$ ratio.

What, then, can we learn about interstellar dust from the study of comets? I suggest two lines of inquiry:

1) Is there really graphite in the interstellar medium after all? Even though it is predicted from thermodynamic calculations, its existence in carbon-rich stars is inferred from observations of dust, and its predicted UV band is present in diffuse clouds, there are nagging doubts. It is worrisome that the UV band is not seen in planetary nebulae. This can be explained if the particles are large enough ($>0.04\mu$; Mathis 1978), but the presence of the band in diffuse clouds requires that they be smaller than that; hence some fragmentation process is necessary. Not only that, but it has been shown that to reproduce the shape of the band observed in diffuse clouds, the graphite particles must be spherical and free from

accreted mantles (Gilra, 1971). Both conditions are hard to accept. Finally, alternative identifications exist, as apparently 2200 \AA is commonly associated with an unpaired π electron in various organic molecules. Most recently, polysaccharides have been suggested in this connection. All these doubts suggest that graphite is actually only a minor constituent of interstellar clouds, and thus, of comets. If this is true, the spectroscopic observations of $^{13}\text{C}/^{12}\text{C}$ in comets are readily understood.

2) Leaving aside graphite, in what form is the carbon in comets? Here the natural choices are CH_4 , already indicated by gas-production studies, and possible Fischer-Tropsch tars. If T_{max} was less than 400° (as seems likely), then such tars could be primordial, and very interesting clues to the conditions under which the dust formed. Also, remember that photolysis is expected to have converted at least some of the icy mantles present into complex organics, perhaps similar to, perhaps different from Fischer-Tropsch tar. This would be of great interest in assessing the history of interstellar dust. Thus, it would be very interesting to get a handle on the form taken by carbon in the nucleus of a comet.

3) As a subsidiary problem, the $^{13}\text{C}/^{12}\text{C}$ ratio is of interest, because the spectroscopic value is uncertain. Also, it would be of interest to extend our knowledge to other constituents like CO_2 , which could originate in a different fraction of carbon.

REFERENCES

- Anders, E. 1971, Ann. Rev. Astron. Astrophys., 9, 1.
- Bless, R.C., Savage, B.D. 1972, Ap. J., 171, 293.
- Cameron, A.G.W. 1973, Space Sci. Rev., 15, 121.
- Field, G.B. 1974, Ap. J., 187, 453.
- Field, G.B., Verschuur, G.L., Ponnampertuma, C. 1978, Cosmic Evolution, (Boston: Houghton Mifflin Co.).
- Gilra, D.P. 1971, Nature, 229, 237.
- Greenberg, J.M., Yench, A.J., Corbett, J.W., Frisch, H.L. 1972, Mém. Soc. Roy. Sci. Liège, Series 6, 3, 425.
- Hoyle, F., Wickramasinghe, N.C. 1962, Mon. Not. R.A.S., 124, 417.
- Klemperer, W.A. 1978, private communication.
- Mathis, J.S. 1978, in Planetary Nebulae, Observations and Theory, ed. Y. Terzian, (Boston: Reidel), p. 281.
- Morton, D.C. 1974, Ap. J., 193, L35.
- Oort, J.H., van de Hulst, H.C. 1946, Bull. Astron. Inst. Neth., 10, 187.
- Snell, R., Tull, R., Vanden Bout, R., Vogt, S. 1977, in CNO Isotopes in Astrophysics, ed. J. Audouze, (Boston: Reidel), p. 85.
- Spitzer, L., Jr. 1978, Physical Processes in the Interstellar Medium, (New York: John Wiley and Sons).
- Townes, C.H. 1977, Observatory, 97, 52.
- Vinogradov, A.P., Kropotova, O.I. Vdovkin, G.P., Grinenko, V.A. 1967, Geochem. Internar., 4, 229.
- Watson, W.G. 1973, Ap. J., 181, L129.
- Whipple, F.W., Heubner, W.F. 1976, Ann. Rev. Astron. Astrophys., 14, 143.